

Peer Review Comments on:

Technical Background Document:  
Mercury Wastes  
Evaluation of Treatment of Bulk Elemental Mercury  
  
and

Technical Background Document:  
Mercury Wastes  
Evaluation of Treatment of Mercury Surrogate Waste

July 9, 2002

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# Review of Mercury Treatability Studies

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## **Review of “Evaluation of Mercury Surrogate Waste”**

### *1. Was the experimental design of the study appropriate?*

The experimental design employed was appropriate in most regards. One problem with the plan was the variability introduced by having vendors prepare the surrogate waste. Data in Appendix C shows that concentrations of potassium, calcium and magnesium were much higher in the surrogates prepared by all vendors than the surrogate prepared by Alter. Furthermore, the concentrations of chloride in surrogate waste prepared by Vendors A, B, and C were much higher than concentrations in the surrogate prepared by Alter and Vendor D. Chloride concentrations are particularly important because of the ability of chloride ions to form soluble complexes with mercury, thereby enhancing its release during leaching tests. Therefore, it is possible that the surrogate waste treated by Vendor D was “easier” to treat, than that treated by the other vendors. Vendor C reported using only about one half of the specified water in preparing its surrogate waste. The effect of reduced water content in the surrogate waste on performance in leaching tests is not clear, but the lack of consistency in surrogate waste preparation is undesirable.

2. *Was the study conducted properly?*

The conduct of the study appears to have been proper.

3. *Were the stated objectives adequately met? (Please note that we are asking you to focus your response on the stated objective listed above and not necessarily on all the objectives stated in the body of each study report.)*

a) Effectiveness of meeting goal of 0.025 mg/L in leaching tests

i) TCLP Test

The treatment process of Vendor A was able to consistently meet the goal (0.025 mg/L) in the TCLP test by substantial margin (concentrations < 0.01 mg/L). There was little, if any, difference between the treated materials in crushed or pellet forms. The ability of this treated waste to meet the goal was confirmed by its performance in the constant pH leaching test (CPLT), in which concentrations were measured below the goal at pH values near that observed in the TCLP.

The treatment process of Vendor B was not able to meet the goal in any samples submitted. This performance was confirmed by the CPLT.

The treatment process of Vendor C was able to meet the treatment goal in all samples submitted (Batch 1, Batch 2). The degree by which the goal was exceeded was greater in Batch 2 than Batch 1. This behavior was confirmed by performance in the CPLT, although concentrations were higher in the CPLT.

The treatment process of Vendor D was able to meet the treatment goal in one sample submitted (Batch 1), but did not meet the treatment goal in another sample (Batch 2). The average TCLP concentration for Batch 2 exceeded the goal, although one sub-sample out of three was lower than the treatment goal. This performance was confirmed by performance of Batch #2 in the CPLT. However, Batch #1 gave a very high concentration in the CPLT near the pH of the TCLP. However, this point does not follow the general trend of the rest of the data for this treated waste or the treated wastes of other vendors, so it appears to be an outlier.

These results support the conclusion that there are existing stabilization technologies that can meet a TCLP goal of 0.025 mg/L in wastes with mercury concentrations well in excess of 260 mg/kg.

#### ii) Constant pH test

Only a few (pH 2, 8, 12) CPLT were replicated, so there is limited data to evaluate the reproducibility of the test procedure. The average relative percentage difference (RPD) for all vendors was 35%, but many individual RPD exceeded 100%. This limits the confidence that can be placed on individual test results, especially when they approach the treatment goal.

The treatment process of Vendor A was able to meet the treatment goal at all pH values except pH 12. All samples meeting the goal did so by a substantial margin (concentration < 0.01 mg/L), except one of the duplicates at pH 8.

The treatment process of Vendor B was not able to meet the treatment goal at any pH values, except for both duplicates of one sample (Phase II, pH 12).

The treatment process of Vendor C was able to meet the goal under some conditions. In general, the goal could be met at higher pH and in Batch #2. Both duplicates met the treatment goal in Batch #2 at pH 8, but only one met the goal in Batch #1 at that pH. Both duplicates met the treatment goal in Batch #2 at pH 12, but neither did in Batch #1 at that pH. The variability in performance between batches shown by the treatment process of Vendor C is not substantially different from that shown by treatment processes of other vendors. However, the treated waste provided by Vendor C produced concentrations in the CPLT that were near the treatment goal, so that there was more variation in whether a particular sample met the goal. The variability in performance of all treated wastes indicates the problems of heterogeneity of the waste and/or variability in application of the treatment process

The treatment process of Vendor D was not able to meet the goal, except at higher pH. At pH 12, three samples met the goal and one sample was at the goal (0.025 mg/L). However, none of the samples at pH 12 exceeded the goal by a substantial margin ( $< 0.01$  mg/L).

b) Comparison of TCLP to constant pH leach test (CPLT).

The CPLT is similar to the TCLP, but it does not duplicate all conditions of the TCLP. In addition to operating at different pH, the CPLT has a longer leaching time (14 days compared to 18 hours), different L/S ratio (20 L/kg dry mass compared to 20 L/kg total mass) and uses a different leaching solution (mixture of nitric acid and/or sodium hydroxide compared to acetic

acid and possibly sodium hydroxide). These differences can lead to observing higher or lower concentrations in the CPLT compared to those measured in the TCLP, even when the CPLT is at the pH observed in the TCLP. Using a L/S ratio defined in terms of dry mass rather than total mass will result in a greater amount of waste being used in the CPLT per unit volume of leachate compared to the TCLP. This would tend to lead to higher concentrations being measured in the CPLT. A longer leaching time in the CPLT would tend to result in the leaching solution approaching more closely to equilibrium conditions with the solids. This could result in higher or lower concentrations being observed, because concentrations in the TCLP test can be increasing or decreasing as the end of the leaching period approaches. Concentrations would tend to continuously increase for components whose solubility is not strongly affected by pH or when the pH of the leaching fluid does not change appreciably. However, concentrations of compounds that are strongly affected by pH would tend to increase initially when pH is low and then decrease as pH rises in the leaching fluid. The presence of nitrate rather than acetic acid/acetate could affect leaching results when one or the other of these compounds forms stronger complexes with a metal being extracted.

The treated waste provided by Vendor A showed concentrations in the TCLP to be similar, but lower than concentrations in the CPLT when interpolated to the pH of the TCLP. However, the constant pH test resulted in some concentrations at other pH values that were much higher than observed for the TCLP at pH values different from that observed in the TCLP.

The treated waste provided by Vendor B showed good agreement in concentrations measured in the TCLP and in the CPLT, when concentrations in the CPLT are interpolated to the pH of the

TCLP. However, the CPLT resulted in some concentrations that were higher and lower than those measured in the TCLP, when measured at pH values different from those observed in the TCLP.

The treated waste provided by Vendor C showed similar concentrations measured in the TCLP and in the CPLT, when concentrations in the CPLT are interpolated to the pH of the TCLP. However, the interpolated concentrations of the CPLT tended to be higher than those in the TCLP. However, the CPLT resulted in some concentrations that were much higher than those observed for the TCLP at pH values different from those observed in the TCLP.

The treated waste provided by Vendor D showed similar concentrations in both leach tests, when compared at the same pH and when the result in the CPLT at pH 10 for Batch #1 is considered an outlier. This point should be considered an outlier because it is much higher than the general trend at other pH values for Batch #1 and very different from that observed for Batch #2 at pH 10. The CPLT resulted in some concentrations that were much higher than those observed for the TCLP at pH values different from those observed in the TCLP.

In general, the two test procedures provided similar results when compared at the same pH. In some cases, the concentrations measured in the TCLP tended to be a little lower than those observed by interpolating concentrations measured in the CPLT to the pH of the TCLP. This could be due to the fact that the TCLP has a higher effective L/S and shorter leaching time than the CPLT. The CPLT also produced concentrations at other pH values that could be much higher than those measured in the TCLP.

## **Review of “Evaluation of Treatment of Bulk Elemental Mercury”**

### *1. Was the experimental design of the study appropriate?*

The experimental design was generally appropriate. One exception was the failure to confirm that waste loadings (elemental mercury loadings) were as reported by the vendors. The report does not present any data supporting the reported waste loadings. The experimental plan calls for mercury concentrations in the waste forms to be determined, but these data are not presented. These concentrations would be a check on the reported waste loadings and should be reported.

Identifying the concentrations of mercury in the waste forms among the raw data in Appendix B is difficult. However, an attempt was made to identify these concentrations and it appears that the mercury contents of treated solids from some vendors were much lower than expected from reported waste loadings. The highest concentration reported for a solid from vendor A (samples 01 to 10, p B-98) is 16,400 mg/kg, compared to a concentration of 330,000 mg/kg expected from the reported waste loading of 33%. The highest concentration found for a solid treated by Vendor B (samples 34 to 43 on p B-154, B-155) is 285,000 mg/kg compared to concentrations of 550,000 mg/kg and 440,000 mg/kg expected for waste loadings of 55% (Phase I) and 44% (Phase II). Other concentrations are reported in this group that are much lower. The highest concentration found for a solid treated by Vendor C is 10,700 mg/kg (samples 9 to 13, p. B-67) compared to a concentration of 201,000 mg/kg expected for a waste loading of 20.1%.

Recoveries of metals from treated wastes are often less than expected. Low recoveries can be the result of inadequate analytical procedures for measuring metals in solids that have been



treated with the intent to reduce the availability of the metal. No information was given concerning the dissolution procedures used on the treated wastes to solubilize mercury prior to analysis. The only procedure specified (SW 846 Method 7470A) is a method for analyzing mercury in aqueous solutions. Therefore, there is no way to determine if the dissolution procedure could be expected to reliably recover mercury. Regardless of the reason for the low recoveries for treated wastes submitted by Vendors A and C, they are so low that they cast doubt on the meaningfulness of the results of leaching tests.

2. *Was the study conducted properly?*

The study was conducted properly, with the exception of assuring that waste loadings were as reported by the vendors.

3. *Were the stated objectives adequately met? (Please note that we are asking you to focus your response on the stated objective listed above and not necessarily on all the objectives stated in the body of each study report.)*

a) Effectiveness of meeting goal of 0.025 mg/L in leaching tests

i) TCLP Test

The treated material prepared by Vendor A did not generally meet the goal of 0.025 mg/L mercury in the TCLP test, although one sample of the palletized material met the goal by a small margin. This behavior was generally confirmed by the CPLT, which showed similar, but generally higher, concentrations interpolated to the pH values measured in the TCLP.

The treated material prepared by Vendor B did meet the treatment goal and it did so by a substantial margin (all concentrations below 0.01 mg/L). The total mercury analysis for the material supplied by this vendor may have been high enough to support the reported waste loading (see response to question 1, above). The behavior in the TCLP was supported by similar behavior in the CPLT near the pH of the TCLP test.

The treated material prepared by Vendor C did meet the TCLP goal, but not by a substantial margin. Concentrations measured in all samples were below 0.025 mg/L, but above 0.010 mg/L. However, the reproducibility was very good, with a coefficient of determination of 9%. The behavior in the TCLP was partially confirmed by the CPLT. The concentration at the TCLP pH (pH 6.7) interpolated from data from the CPLT was similar, but somewhat higher. The interpolated concentration in the CPLT was strongly influenced by the CPLT data point at pH 6, which was somewhat lower than those measured at pH 4 and pH 8. The ability of this treated material to reliably pass the TCLP goal is also brought into question by indications that concentrations of total mercury may have been measured in the treated material that are much lower than what would be expected from the reported waste loading (see response to question 1, above).

#### ii) Constant pH test

The treated material prepared by Vendor A did not meet the goal of 0.025 mg/L in the CPLT except at pH 2 (pellets and crushed samples) and pH 11 (pellets). The behavior in the CPLT was generally confirmed by that in the TCLP when concentrations are compared near the pH of the

TCLP. However, interpolated concentrations in the CPLT tended to be generally higher than those measured in the TCLP.

The treated material prepared by Vendor B did meet the goal in the CPLT, except at pH 12. The behavior in the CPLT was generally confirmed by that in the TCLP when compared by interpolating CPLT data to the pH of the TCLP.

The treated material prepared by Vendor C generally did not meet the goal in the CPLT. Two samples at pH 12 had concentrations (0.0251 mg/L and 0.0249 mg/L) that were substantially the same as the treatment goal. The concentrations measured in the TCLP at pH 6.7 were similar to that measured in the CPLT at pH 6, but substantially lower than that measured at pH 8.

## **General Comments**

1. *Are you aware of any other data/studies that are relevant to the assessment of stabilized mercury-bearing wastes and the behavior of these wastes in the environment?*

The following articles are relevant to this topic.

“Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement”, Zhang, Jian; Bishop, Paul L. *Journal of Hazardous Materials* (2002), 92(2), 199-212.

“Sulfide-induced stabilization and leachability studies of mercury containing wastes”, Piao, Haishan; Bishop, Paul, Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002 (2002), ENVR-207.

“Phosphate-induced mercury stabilization”, Zhang, Jian; Bishop, Paul L., Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2001), 41(1), 422-424.

“Sulfide-induced mercury stabilization”, Piao, Haishan; Bishop, Paul L., Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2001), 41(1), 428-431.

“Stabilization of radioactively contaminated elemental mercury wastes”, Stewart, Robin; Broderick, Tom; Litz, John; Brown, Cliff; Faucette, Andrea., Proceedings of the

- International Conference on Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management, Denver, Sept. 13-18, 1998 (1998), 3 33-36.
- “Mercury stabilization in chemically bonded phosphate ceramics”, Wagh, Arun S.; Jeong, Seung-Young; Singh, Dileep, *Ceramic Transactions* (1998), 87(Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries III), 63-73.
- “A Framework for Risk Assessment of Disposal of Wastes Treated by Solidification/Stabilization”, Batchelor, B., *Environmental Engineering Science*, 14(1): 3-13, 1997.
- “A study of immobilization of four heavy metals by solidification/stabilization with Portland cement”, Susan A. Trussell, Ph.D. Dissertation, Texas A&M University, College Station, Texas, 1994.
- “Immobilization of chromium and mercury from industrial wastes”, Wasay, S. A.; Das, H. A. , *J. Environ. Sci. Health, Part A* (1993), A28(2), 285-97.
- Chemical Fixation and Solidification of Hazardous Wastes*, Jesse R. Conner, Van Nostrand Reinhold, New York, 1990.
- “An investigation of mercury solidification and stabilization in portland cement using x-ray photoelectron spectroscopy and energy dispersive spectroscopy”, McWhinney, Hylton G.; Cocke, David L.; Balke, Karl; Ortego, J. Dale., *Cem. Concr. Res.* (1990), 20(1), 79-91.
- “Studies of zinc, cadmium and mercury stabilization in OPC/PFA mixtures”, Poon, C. S.; Perry, R., *Mater. Res. Soc. Symp. Proc.* (1987), 86(Fly Ash Coal Convers. By-Prod.), 67-76.
- “Permeability study on the cement based solidification process for the disposal of hazardous wastes”, Poon, C. S.; Clark, A. I.; Perry, R.; Barker, A. P.; Barnes, P., *Cem. Concr. Res.* (1986), 16(2), 161-72.
- “Mechanisms of metal fixation and leaching by cement based fixation processes”, Poon, C. S.; Clark, A. I.; Peters, C. J.; Perry, R., *Waste Manage. Res.* (1985), 3(2), 127-42.
- “Mechanisms of metal stabilization by cement based fixation processes”, Poon, C. S.; Peters, C. J.; Perry, R.; Barnes, P.; Barker, A. P., *Sci. Total Environ.* (1985), 41(1), 55-71.

Additionally, a database is being prepared that will contain information on many characteristics of wastes. This will include those containing mercury. The final report has not been prepared but information is available at <http://www.concrete.cv.ic.ac.uk/iscowaa/nnapics/intro.html>

2. *With regard to the disposal of treated mercury wastes, are additional studies warranted for other factors that impact solubility (e.g., liquid/solid ratio, redox conditions, leachate composition) or affect ability to leach, such as use of macroencapsulation? If you believe that additional studies are needed, please explain why.*

These studies have adequately demonstrated that a goal of 0.025 mg/L in the TCLP can be met by existing stabilization technologies, both for a surrogate waste containing various forms of mercury at a total concentration of 5,000 mg/kg and for elemental mercury. However, meeting this goal does not insure that adequate protection of human health and the environment is assured for all conditions of waste disposal. However, this statement is not limited to mercury wastes, but is a limitation of the TCLP for all hazardous constituents. Therefore, additional studies are not warranted to determine if existing technologies can meet a TCLP goal of 0.025 mg/L for wastes that contain mercury at concentrations above 260 mg/kg. However, additional studies are warranted to develop characterization methods and analytical techniques that will insure safe disposal of hazardous wastes containing toxic materials including mercury under a range of site-specific disposal conditions.

3. *Do you agree that the following statements are supported by the research results?*

a. *Site specific disposal conditions must be considered along with appropriate treatment technology as decisions are made about disposal of mercury wastes.*

These research results do support this statement, because they demonstrate that pH can have an important impact on the amount of mercury leached from treated wastes. The pH of a leaching fluid can be very different under different disposal conditions. However, the research results do not prove the statement, because there could be conditions under which a waste could be characterized so that site-specific disposal conditions would not be required to insure a reasonable degree of confidence in protection of human health and the environment.

*b. The presence of chloride ions in a given disposal environment may significantly impact the release from a treated waste form (mercury selenide).*

This statement is supported by the research results, because a leaching solution with 500 mg/L chloride did result in higher concentrations of mercury being leached at pH 7 and 10. However, the data reported is not sufficient to conclude that chloride will (rather than may) significantly impact release of mercury under a range of disposal conditions. Sufficient data exists on formation of mercury-chloride soluble complexes to strongly suggest that chloride will tend to increase mercury release, but specific conclusions on the impact of particular levels of chloride in different disposal scenarios would require additional research.

4. *Any additional comments?*

The following corrections should be made to the reports.

a) “Evaluation of Mercury Surrogate Waste”

(various places) The relationship of ALTER and the University of Cincinnati should be clarified.

It appears that the two are used interchangeably. This comment also applies to “Evaluation of Treatment of Bulk Elemental Mercury”.

(p. 2-5, bullet 3) should be “< 260 ppm”

(p. 3-4, line 5 from bottom and elsewhere) Provide units for liquid/solid ratio. This comment also applies to “Evaluation of Treatment of Bulk Elemental Mercury”.

(p. 5-1, Table 5-1 and others) Percentages should be reported with no more significant digits than the measurements upon which they are based. This comment also applies to “Evaluation of Treatment of Bulk Elemental Mercury”.

(p. 5-1, Table 5-1 and others) The leaching fluid used in the TCLP tests should be specified. This comment also applies to “Evaluation of Treatment of Bulk Elemental Mercury”.

(p. 5-5, Table 5-4, columns 2,3,6,7) Replace “3/4” with blank or other indication that presenting the percent leached is not appropriate for a blank.

b) “Evaluation of Treatment of Bulk Elemental Mercury”

(p. 3-2) It would be helpful to the reader to make more clear here that the “waste” being treated is elemental mercury.

(p. 5-4, Table 5-3) Standard deviation of TCLP results for Phase II should be 0.00160.

(p. 5-6, Figure 5-3) TCLP data are missing from this figure.